



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 634 481 A1

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 93870145.5

⑮ Int. Cl.⁶: **C11D 3/39, C11D 3/22**

⑯ Date of filing: **14.07.93**

⑰ Date of publication of application:
18.01.95 Bulletin 95/03

⑲ Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE**

⑳ Applicant: **THE PROCTER & GAMBLE
COMPANY
One Procter & Gamble Plaza
Cincinnati
Ohio 45202 (US)**

㉑ Inventor: **Baillely, Gerard Marcel
14 Low Gosforth Court
Gosforth,
Newcastle upon Tyne NE3 5QU (GB)**

㉒ Representative: **Canonici, Jean-Jacques et al
Procter & Gamble European Technical
Center N.V.
Temselaan 100
B-1853 Strombeek-Bever (BE)**

㉓ Detergent compositions.

㉔ There is provided a low temperature process for washing laundry in a domestic washing machine and detergent compositions suitable for use in such a process. In the process of the invention an effective amount of a laundry detergent composition is introduced into the wash liquor during the wash and the process is conducted at a temperature of no more than 50 °C, the laundry preferably comprising hydrophobic materials such as polyester or polycotton. The detergent composition comprising an alkali metal percarbonate and one or more non-ionic cellulose derivatives. The washing process of the invention leads to improved whiteness benefits and reduced dispensing problems when compared with processes in which detergent compositions are used which contain perborate as a bleaching agent instead of percarbonate.

EP 0 634 481 A1

This invention relates to a low temperature process for washing laundry in a domestic washing machine and to detergent compositions suitable for use in such a process which comprise alkali metal percarbonate and non-ionic cellulose derivatives.

Non-ionic cellulose derivatives, in particular cellulose ethers, are known to be useful as anti-redeposition agents. They are particularly useful in preventing the redeposition of greasy stains on hydrophobic fabrics such as polyester or polycotton. Redeposition is believed to be prevented at least in part by the formation of a release coating of the non-ionic cellulose derivatives on the hydrophobic fabric.

It is known to provide laundry detergent compositions incorporating an inorganic perhydrate salt as a source of oxygen bleach. The inorganic perhydrate bleach most widely used in laundry detergent composition is sodium perborate in the form of either the monohydrate or tetrahydrate.

It is believed that on dissolution in water, perborate gives borate ions and that these borate ions are capable of forming ionic complexes with α (vicinal) diols such as cellulose derivatives. Such ionic complexes have increased solubility over the non-complexed cellulose derivative and their deposition onto hydrophobic fabrics is hampered. Hence achievement of brightness by prevention of redeposition of greasy stains is hindered and in order to achieve adequate performance it is often found necessary to increase the percentage of cellulose derivative in the detergent composition.

It is desirable to keep levels of cellulose derivative to a minimum, both for cost reasons and because high levels can lead to dispensing and formulation problems.

According to the invention there is provided a laundry detergent composition comprising:

- 20 (a) an alkali metal percarbonate
- (b) one or more non-ionic cellulose derivatives.

According to the invention there is also provided a process of washing laundry, preferably in a domestic washing machine, in which an effective amount of a laundry detergent composition of the invention is introduced into the wash liquor during the wash, wherein the process is conducted at a temperature of no 25 more than 50 °C. The non-ionic cellulose derivative preferably remains substantially unionised during the wash.

It has been found that detergent compositions comprising percarbonate and cellulose derivatives give superior anti-redeposition and whiteness/brightness performance over detergent compositions comprising perborate and cellulose derivatives or cellulose derivative alone. It seems that percarbonate does not hinder 30 the deposition of cellulose derivative onto hydrophobic fabrics. This is probably due to the percarbonate not causing ionisation of the diol in the cellulose. Irrespective of the mechanism, it is surprisingly possible to reduce levels of cellulose derivatives in detergent compositions and to reduce dispensing problems, or to obtain better anti-redeposition properties, by using percarbonate instead of perborate.

The non-ionic cellulose derivative is preferably a cellulose ether. Cellulose ethers which are particularly 35 useful according to the invention include hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose and mixtures thereof. Hydroxyethyl cellulose is particularly preferred.

It is desirable that the non-ionic cellulose derivative be present in the detergent composition in an amount which is as low as possible whilst retaining adequate anti-redeposition and whiteness performance. It is generally present in an amount of not more than 3% by weight of total composition, preferably not 40 more than 1.5%, more preferably not more than 1% by weight of total composition.

The alkali metal percarbonate used is preferably sodium or potassium percarbonate, more preferably sodium percarbonate. The percarbonate is generally in particulate form. The percarbonate particles generally have a mean particle diameter of 150 to 1200 μm , preferably 300 to 900 μm . The particles of percarbonate may be coated or uncoated. If they are coated this is preferably with a water-soluble coating. 45 Suitable coating materials include the alkali or alkaline earth metal carbonates; the alkali or alkaline earth metal sulphates; the mixed salts of alkali or alkaline earth metal sulphates and carbonates; the mixed salts of alkali or alkaline earth metal chlorides and carbonates; the mixed salts of alkali or alkaline earth metal nitrates and carbonates. Suitable coatings together with coating processes have been described in GB 1,466,799.

50 The percarbonate may be present in the detergent composition in any of the proportions used conventionally. The benefits of the invention are shown in particular by compositions containing a large proportion of oxygen-releasing bleaching agent, for instance 9% or more by weight. Since it has been found that it is advantageous to replace perborate with percarbonate and that hindrance of performance is particularly noticeable in compositions containing high proportions of perborate, the benefits of the invention 55 will be felt in particular in equivalent formulations containing percarbonate. Thus the advantages of the invention are most noticeable in compositions containing percarbonate in an amount of 9% or more by weight of total composition.

In the process of the invention the non-ionic cellulose derivative is thought to remain substantially unionised throughout the wash. A certain very small amount of ionisation may occur naturally on introduction of the cellulose derivative into the wash liquor; however the degree of such ionisation is extremely small and the resulting concentration of ionised cellulose derivative in the wash liquor will also be 5 extremely small. Ionisation does not occur to the extent that it has been found to do when perborate bleach or other sources of borate ion are introduced into the wash liquor.

The process of the invention is conducted at a temperature of no higher than 50 °C. It is preferably conducted at a temperature of no higher than 45 °C, more preferably no higher than 40 °C, most preferably at a temperature of 10 to 35 °C.

10 The process of the invention is particularly effective when the laundry comprises synthetic fabrics, including hydrophobic fabrics such as polyesters and polycottons.

The granular detergent compositions in accord with the invention may comprise from 1% to 40% by weight of the composition, preferably from 2% to 15% by weight, most preferably from 3% to 10% by weight of additional bleaching agents, selected from peroxyacid bleach precursors and organic peroxyacids 15 and mixtures thereof.

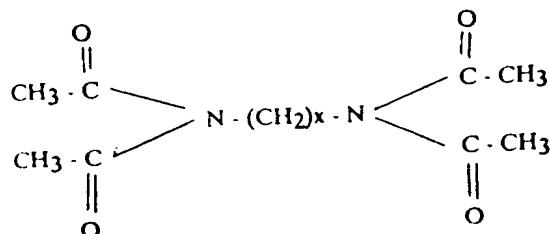
Peroxyacid bleach activators (bleach precursors) as additional bleaching components in accord with the invention can be selected from a wide range of classes and are preferably those containing one or more N- or O- acyl groups.

Suitable classes include anhydrides, esters, amides and acylated derivatives of imidazoles and oximes, 20 and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836 988, 864 798, 1 147 871 and 2 143 231 and amides such as are disclosed in GB-A-855 735 and 1 246 338.

Particularly preferred bleach activator compounds as additional bleaching components in accord with the invention are the N,N,N',N' tetra acetylated compounds of formula

25

30



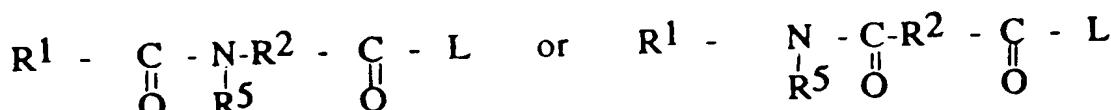
35

where x can be 0 or an integer between 1 and 6.

Examples include tetra acetyl methylene diamine (TAMD) in which x = 1, tetra acetyl ethylene diamine (TAED) in which x = 2 and Tetraacetyl hexylene diamine (TAHD) in which x = 6. These and analogous compounds are described in GB-A-907 356. The most preferred peroxyacid bleach activator as an 40 additional bleaching component is TAED.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:

45



50 wherein R¹ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from about 6 to 12 carbon atoms. R² preferably contains from about 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both 55 and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms total. Amide substituted bleach activator

compounds of this type are described in EP-A-0170386.

Other peroxyacid bleach activator compounds include sodium nonanoyloxy benzene sulfonate, sodium trimethyl hexanoyloxy benzene sulfonate, sodium acetoxy benzene sulfonate and sodium benzyloxy benzene sulfonate as disclosed in, for example, EP-A-0341947.

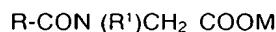
5 The compositions of the invention in addition comprise, in general terms, those ingredients conventionally found in laundry detergent products.

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, amphoteric and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. A list of suitable cationic surfactants is 10 given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Mixtures of anionic surfactants are suitable herein, particularly blends of sulphate, sulphonate and/or carboxylate surfactants. Mixtures of sulphonate and sulphate surfactants are normally employed in a sulphonate to sulphate weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1.

15 Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source, preferably from a C₁₆-C₁₈ fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants in such sulphonate sulphate mixtures are alkyl sulphates having from 12 to 22, preferably 16 to 18 carbon atoms in the alkyl radical. Another useful 20 surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. One such system comprises a mixture of C₁₄-C₁₅ alkyl sulphate and C₁₆-C₁₈ alkyl sulphate in a weight ratio of C₁₄-C₁₅ : C₁₆-C₁₈ of from 3:1 to 1:1. The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. The cation in each instance is again an alkali metal, 25 preferably sodium.

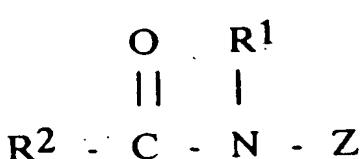
Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula



30 wherein R is a C₉-C₁₇ linear or branched alkyl or alkenyl C group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, cocoyl (C₁₂-C₁₄), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

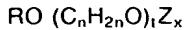
One class of nonionic surfactants useful in the present invention comprises condensates of ethylene 35 oxide with a hydrophobic moiety, providing surfactants having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5 in which the hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature. Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per 40 mole of alcohol and the C₁₂-C₁₄ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

A further preferred class of nonionic surfactants comprises polyhydroxy fatty acid amides of general formula:



where R₁ is H, a C₁-C₄ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or mixtures thereof, R₂ is a C₅-C₃₁ hydrocarbyl and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least three hydroxy groups directly connected to the chain, or an alkoxyated derivative thereof. In preferred members 55 of this class the polyhydroxy hydrocarbyl moiety is derived from glucose or maltose or mixtures thereof and the R₂ group is a C₁₁-C₁₉ alkyl or alkenyl moiety as the R₁ group. Compositions incorporating such highly preferred polyhydroxy fatty acid amides are disclosed in the copending British Application No. 9113139 filed June 18 1991.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



5 wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine 10 oxides are selected from mono C₈-C₂₀, preferably C₁₀-C₁₄ -alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium 15 surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

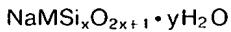
The detergent compositions generally comprise from 3% to 35% by weight of the composition of surfactant but more usually comprise from 5% to 25% by weight, more preferably from 10% to 25% by weight.

Combinations of surfactant types are preferred, more especially anionic-nonionic and also anionic-20 nonionic-cationic blends. Particularly preferred combinations are described in GB-A-2040987, GB 9113139 and EP-A-0087914. Although the surfactants can be incorporated into the compositions as mixtures, it is preferable to control the point of addition of each surfactant in order to optimise the physical characteristics of the composition and avoid processing problems. Preferred modes and orders of surfactant addition are described hereinafter.

25 The granular detergent compositions in accord with the invention also preferably comprise a detergent builder system comprising one or more detergent builders, most preferably non-phosphate detergent builders. The detergent composition as a whole is preferably free of phosphate. These can include, but are not restricted to alkali metal carbonates, bicarbonates, calcium carbonate, calcium bicarbonate, silicates, aluminosilicates, monomeric and oligomeric polycarboxylates, homo or copolymeric polycarboxylic acids or 30 their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, and mixtures of any of the foregoing. The builder system is present in an amount of from 1% to 80% by weight of the composition, preferably from 25% to 60% by weight, more preferably from 30% to 60% by weight.

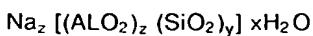
Suitable silicates are those having an SiO₂ : Na₂O ratio in the range from 1.6 to 3.4, the so-called 35 amorphous silicates of SiO₂ : Na₂O ratios from 2.0 to 2.8 being preferred. These materials can be added at various points of the manufacturing process, such as in a slurry of components that are spray dried or in the form of an aqueous solution serving as agglomerating agent for other solid components, or, where the silicates are themselves in particulate form, as solids to the other particulate components of the composition. However, for compositions in which the percentage of spray dried components is low ie 30%, it is 40 preferred to include the amorphous silicate in the spray-dried components.

Within the silicate class, highly preferred materials are crystalline layered sodium silicates of general formula



45 wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and 50 preferred examples of this formula comprise the α , β , γ and δ forms of Na₂Si₂O₅. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is -Na₂Si₂O₅, NaSKS-6. Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

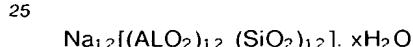
Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate 55 zolites have the unit cell formula



wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The above aluminosilicate ion exchange materials are further characterised by a particle size diameter 5 of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 200 mg equivalent of CaCO_3 10 water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of CaCO_3 /litre minute/(g/litre) [2 grains Ca^{++} /gallon/minute/(gram/gallon)] of aluminosilicate (anhydrous basis), and which generally lies within the range of from 130 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [2 grains/gallon/minute/(gram/gallon)] to 390 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [6 grains/gallon/minute/(gram/gallon)], 15 based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [4 grains/gallon/minute/(gram/gallon)].

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available 20 and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite MAP, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula

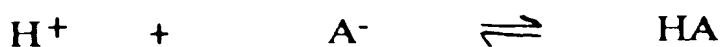


wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5\text{H}_2\text{O}$.

30 Suitable water-soluble monomeric and oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably between 4 and 7.5.

The logarithmic acidity constant is defined by reference to the equilibrium

35



40

where A^- is the singly ionized anion of the carboxylate builder salt.

The equilibrium constant is therefore for dilute solutions given by the expression

45

$$K_1 = \frac{[\text{HA}]}{[\text{H}^+][\text{A}^-]}$$

50

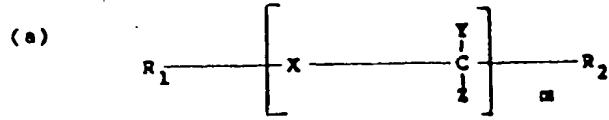
and $\text{pK}_1 = \log_{10} K_1$.

For the purposes of this specification, acidity constants are defined as 25 °C and at zero ionic strength. Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, the Chemical Society, London): where doubt arises they are determined by potentiometric titration using a glass electrode.

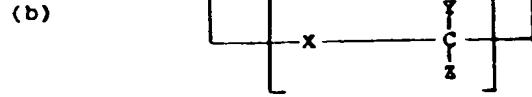
The carboxylate or polycarboxylate builders can be monomeric or oligomeric in type although monomeric carboxylates are generally preferred for reasons of cost and performance.

Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates having the general formulae

5



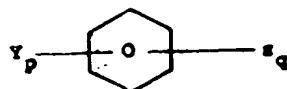
10



15

or

(c)



20

wherein R₁ represents H, C₁₋₃₀ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo- or phosphono groups or attached to a polyethyleneoxy moiety containing up to 20 ethyleneoxy groups; R₂ represents H, C₁₋₄ alkyl, alkenyl or hydroxy alkyl, or alkaryl, sulfo, or phosphono groups; X represents a single bond; O; S; SO; or NR₁; Y represents H; carboxy; hydroxy; carboxymethoxy; or C₁₋₃₀ alkyl or alkenyl optionally substituted by hydroxy or carboxy groups; Z represents H; or carboxy; m is an integer from 1 to 10; n is an integer from 3 to 6; p, q are integers from 0 to 6, p + q being from 1 to 6; and wherein, X, Y, and Z each have the same or different representations when repeated in a given molecular formula, and wherein at least one Y or Z in a molecule contain a carboxyl group.

Suitable carboxylates containing one carboxy group include lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegungsschrift 2,446,686, and 2,446,687 and US Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitlates and citraconates as well as succinate derivatives such as the carboxymethoxy succinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829,1, and the 1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in US Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis, cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, eg citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems useful in the present invention.

Other suitable water soluble organic salts are the homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other

by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Within the preferred compositions, a sodium aluminosilicate such as Zeolite A will comprise from 20% to 60% by weight of the total amount of builder, a monomeric or oligomeric carboxylate will comprise from 10% to 30% by weight of the total amount of builder and a crystalline layered silicate will comprise from 10% to 65% by weight of the total amount of builder. In such compositions, the builder ingredient 10 preferably also incorporates a combination of auxiliary inorganic and organic builders such as sodium carbonate and maleic anhydride/acrylic acid copolymers in amounts of up to 35% by weight of the total builder.

The compositions of the invention may include a low level of heavy metal sequestrant. Preferred heavy metal sequestrants for inclusion in the detergent compositions of the invention include the organic phosphonates, including amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates. Such phosphonate compounds may be present either in their acid form or as a complex of either an alkali or alkaline metal ion, the molar ratio of said metal ion to said phosphonate compound being at least 1 : 1. Such complexes are described in US-A-4,259,200. 20 Preferably, the organic phosphonate compounds are in the form of their magnesium salt.

Organic phosphonate compounds, and mixtures thereof, may be present in the detergent compositions of the invention at levels of from 0.05% to 10% by weight of the composition, preferably 0.1% to 2% by weight, most preferably 0.2% to 0.6% by weight.

Compositions in accordance with the invention can also contain other optional detergent ingredients. 25 Further anti-redeposition and soil-suspension agents, optical brighteners, soil release agents, dyes and pigments are examples of such optional ingredients and can be added in varying amounts as desired.

Anti-redeposition and soil-suspension agents suitable herein (other than the cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, already mentioned) include homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include copolymers of maleic 30 anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000 - 10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of 35 from 0.20% to 5%, more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance of clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2¹ disulphonate, disodium 4, 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2:2¹ - disulphonate, disodium 4, 4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2¹ - disulphonate, monosodium 4¹, 4¹¹ - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4, 4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethyl ylamino)-s-triazin-6-ylamino)stilbene-2,2¹ - disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2¹ disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethyl ylamino)-s-triazin-6-ylamino)stilbene-2,2¹ disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹, 2¹:4,5)-1,2,3 - triazole-2¹¹-sulphonate.

Soil-release agents useful in composition of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 50 and European Published Patent Application No. 0272033. A particular preferred polymer in accordance with EP-A-0272033 has the formula



55 where PEG is -(OC₂H₄)_{0,75}, PO is (OC₃H₆O) and T is (pCOC₆H₄CO).

Certain polymeric materials such as polyvinyl pyrrolidones typically of MWt 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously 5 releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the 10 silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

15 A preferred silicone suds controlling agent is disclosed in Bartolotta et al US Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

20 The suds suppressor described above are normally employed at levels of from 0.001% to 0.5% by weight of the composition, preferably from 0.01% to 0.1% by weight.

The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation 25 of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al US Patent No. 3,933,672.

An other optional ingredient useful in the present invention is one or more enzymes.

30 Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase and Savinase by Novo Industries A/S (Denmark) and Maxalase by International Bio-Synthetics, Inc. (The 35 Netherlands).

Preferred amylases include, for example, -amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,296,839 (Novo). Preferred commercially available amylases include for example, Rapidase, sold by International Bio-Synthetics Inc. and Termamyl, sold by Novo Industries A/S.

An especially preferred lipase enzyme is manufactured and sold by Novo Industries A/S (Denmark) 40 under the trade name Lipolase (Biotechnology Newswatch, 7 March 1988, page 6) and mentioned along with other suitable lipases in EP-A-0258068 (Novo).

Fabric softening agents can also be incorporated into laundry detergent compositions. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water insoluble tertiary amines as 45 disclosed in GB-A-1514276 and EP-B-0011340.

Their combination with mono C₁₂-C₁₄ quaternary ammonium salts is disclosed in EP-B-0026527 and 528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in EP-B-0242919. Additional organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

50 Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at 55 levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

A feature of the compositions of the present invention is that they may be of relatively high density in comparison with conventional laundry detergent compositions. Such high density compositions have become known as concentrated products and are characterised by a bulk density of at least 650 g/litre, more usually at least 700 g/litre and more preferably in excess of 800 g/litre. Bulk density is measured by 5 means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, 10 an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in 15 g/litre. Replicate measurements are made as required.

Compositions of the present invention may incorporate at least one multi-ingredient component ie they may not comprise compositions formed merely by dry-mixing all of the individual ingredients. Compositions in which each individual ingredient is dry-mixed are generally dusty, slow to dissolve and also tend to cake and develop poor particle flow characteristics in storage.

20 The compositions of the invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and preferred methods involve combinations of these techniques. A preferred method of making the composition involves a combination of spray drying, agglomeration in a high speed mixer and dry mixing.

Preferred detergent compositions in accordance with the invention comprise at least two particulate 25 multi-ingredient components. The first component comprises at least 15%, conventionally from 25% to 50%, but more preferably no more than 35% by weight of the composition and the second component from 1% to 50%, more preferably 10% to 40% by weight of the composition.

In a preferred embodiment of the invention, one multi-ingredient component comprises an agglomerate 30 of non-spray-dried ingredients together with a second multi-ingredient component comprising a spray-dried powder.

The first component comprises a particulate incorporating an anionic surfactant in an amount of from 35 0.75% to 40% by weight of the powder and one or more inorganic and/or organic salts in an amount of from 99.25% to 60% by weight of the powder. The particulate can have any suitable form such as granules, flakes, prills, marumes or noodles but is preferably granular. The granules themselves may be agglomerates formed by pan or drum agglomeration or by in-line mixers but are customarily spray dried particles produced by atomising an aqueous slurry of the ingredients in a hot air stream which removes most of the water. The spray dried granules are then subjected to densification steps, eg by high speed cutter mixers and/or compacting mills, to increase density before being reagglomerated. For illustrative purposes, the first component is described hereinafter as a spray dried powder.

40 Suitable anionic surfactants for the purposes of the first component have been found to be slowly dissolving linear alkyl sulfate salts in which the alkyl group has an average of from 16 to 22 carbon atoms, and linear alkyl carboxylate salts in which the alkyl group has an average of from 16 to 24 carbon atoms.

The alkyl groups for both types of surfactant are preferably derived from natural fats such as tallow. Shorter chain alkyl sulfates or carboxylates, in which the alkyl group is derived from sources comprising a 45 mixture of alkyl moieties more than 40% of which contain 14 or less carbon atoms, are less suitable as they cause the first component to form a gel like mass during dissolution.

The level of anionic surfactant in the spray dried powder forming the first component is from 0.75% to 40% by weight, more usually 2.5% to 25%, preferably from 3% to 20% and most preferably from 5% to 50% by weight. Water-soluble surfactants such as linear alkyl benzene sulphonates or C₁₄-C₁₅ alkyl sulphates can be included or alternatively may be applied subsequently to the spray dried powder by spray on.

The other major ingredient of the spray dried powder is one or more inorganic or organic salts that 55 provide the crystalline structure for the granules. The inorganic and/or organic salts may be water-soluble or water-insoluble, the latter type being comprised by the, or the major part of the, water-insoluble builders where these form part of the builder ingredient. Suitable water soluble inorganic salts include the alkali metal carbonates and bicarbonates. Alkali metal silicates other than crystalline layered silicates can also be present in the spray dried granule provided that aluminosilicate does not form part of the spray dried component.

Where an aluminosilicate zeolite forms the, or part of the, builder ingredient, it is preferred that it is not added directly by dry mixing to the other components, but is incorporated into the multi-ingredient component(s). Where incorporation of the zeolite takes place in the spray-dried granule, any silicate present should not form part of the spray-dried granule. In these circumstances incorporation of the silicate can be 5 achieved in several ways, eg by producing a separate silicate-containing spray-dried particulate, by incorporating the silicate into an agglomerate of other ingredients, or more preferably by adding the silicate as a dry mixed solid ingredient.

The first component can also include up to 15% by weight of miscellaneous ingredients such as brighteners, anti-re-deposition agents, which may include non-ionic cellulose derivatives, photoactivated 10 bleaches and heavy metal sequestering agents. Where the first component is a spray dried powder it will normally be dried to a moisture content of from 7% to 11% by weight, more preferably from 8% to 10% by weight of the spray dried powder. Moisture contents of powders produced by other processes such as 15 agglomeration may be lower and can be in the range 1-10% by weight.

The particle size of the first component is conventional and preferably not more than 5% by weight 20 should be above 1.4 mm, while not more than 10% by weight should be less than 0.15 mm in maximum dimension. Preferably at least 60%, and most preferably at least 80%, by weight of the powder lies between 0.9 mm and 0.25 mm in size. For spray dried powders, the bulk density of the particles from the spray drying tower is conventionally in the range from 540 to 600 g/litre and this is then enhanced by further processing steps such as size reduction in a high speed cutter/mixer followed by compaction.

25 Alternatively, processes other than spray drying may be used to form a high density particulate directly.

A second component of a preferred composition in accordance with the invention is another multi-ingredient particulate containing a water soluble surfactant.

This water-soluble surfactant may be anionic, nonionic, cationic or semipolar in type or a mixture of any 30 of these. Suitable surfactants are listed hereinbefore but preferred surfactants are C₁₄-C₁₅ alkyl sulphates linear C₁₁-C₁₅ alkyl benzene sulphonates and fatty C₁₄-C₁₈ methyl ester sulphonates. The second component may have any suitable physical form ie; it may take the form of flakes, prills, marumes, noodles, ribbons or granules which may be spray-dried or non spray-dried agglomerates. Although the second component could in theory comprise the water soluble surfactant on its own, in practice at least one organic or inorganic salt is included to facilitate processing. This provides a degree of crystallinity, and hence 35 acceptable flow characteristics, to the particulate and may be any one or more of the organic or inorganic salts present in the first component.

The particle size range of the second component is not critical but should be such as to obviate segregation from the particles of the first component when blended therewith. Thus not more than 5% by weight should be above 1.4 mm while not more than 10% should be less than 0.15 mm in maximum 40 dimension.

The bulk density of the second component will be a function of its mode of preparation. However, the preferred form of the second component is a mechanically mixed agglomerate which may be made by adding the ingredients dry or with an agglomerating agent to a pan agglomerator, Z blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV 29 Chroomstraat 8211 AS, 45 Lelystad, Netherlands and Gebruder Lüdige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050 FRG. By this means the second component can be given a bulk density in the range from 650 g/litre to 1190 g/litre more preferably from 750 g/litre to 850 g/litre.

Preferred compositions include a level of alkali metal carbonate in the second component corresponding to an amount of from 3% to 15% by weight of the composition, more preferably from 5% to 12% by 45 weight. This will preferably provide a level of carbonate in the second component of from 20% to 40% by weight.

A highly preferred ingredient of the second component is also a hydrated water insoluble aluminosilicate ion exchange material of the synthetic zeolite type, described hereinbefore, present at from 10% to 35% by weight of the second component. The amount of water insoluble aluminosilicate material 50 incorporated in this way is from 1% to 10% by weight of the composition, more preferably from 2% to 8% by weight.

In one process for preparing the second component, the surfactant salt is formed in situ in an inline mixer. The liquid acid form of the surfactant is added to a mixture of particulate anhydrous sodium 55 carbonate and hydrated sodium aluminosilicate in a continuous high speed blender such as a Lüdige C6 mixer and neutralised to form the surfactant salt whilst maintaining the particulate nature of the mixture. The resultant agglomerated mixture forms the second component which is then added to other components of the product. In a variant of this process, the surfactant salt is pre-neutralised and added as a viscous paste to the mixture of the other ingredients. In this variant, the mixer serves merely to agglomerate the

ingredients to form the second component.

In a particularly preferred process for making compositions in accordance with the invention, part of the spray dried product comprising the first granular component is diverted and subjected to a low level of nonionic surfactant spray-on before being reblended with the remainder. The second granular component is made using the preferred process described above. The first and second components together with other dry mix ingredients such as any carboxylate chelating agent, the sodium percarbonate bleach, bleach activator, soil-release polymer, silicate of conventional or crystalline layered type and enzyme are then fed to a conveyor belt, from which they are transferred to a horizontally rotating drum in which perfume and silicone suds suppressor are sprayed on to the product. In highly preferred compositions, a further drum mixing step is employed in which a low (approx. 2% by weight) level of finely divided crystalline material is introduced to increase density and improve granular flow characteristics. This material should not however be an aluminosilicate zeolite builder as it has been found that zeolite builders present in discrete particulate form in the product have an adverse effect on percarbonate stability.

In a preferred washing process according to the invention a dispensing device containing an effective amount of granular detergent product is introduced into the drum of a washing machine before the commencement of the wash cycle. What constitutes an effective amount of granular detergent product for use in the process described here in above will depend on the volume and weight of the laundry load to be washed. Use of between 70-150 g of product would be typical for a normal wash load of between 2-6 kg of averagely soiled laundry.

The dispensing device is a container for the detergent product which is used to deliver the product directly into the drum of the washing machine. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in a washing process as hereinbefore described.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its immersion in the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the automatic washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use in accord with the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette".

Another preferred means of carrying out the process of the invention is to introduce the composition into the liquid surrounding the fabrics that are in the drum via a reusable dispensing device having walls that are permeable to liquid but impermeable to the solid composition.

Especially preferred devices of this kind are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene

or polypropylene.

The detergent compositions of the invention are illustrated in the following non limiting examples in which all percentages are on a weight basis unless otherwise stated.

In the detergent compositions, the abbreviated component identifications have the following meanings :

5	LAS	: Sodium linear C ₁₂ alkyl benzene sulphonate
	C ₁₆₋₁₈ AS	: Sodium C ₁₆ -C ₁₈ alkyl sulphate
	C ₁₄₋₁₅ AS	: Sodium C ₁₄ -C ₁₅ alkyl sulphate
	C ₁₄₋₁₅ AE7	: A C ₁₄ -C ₁₅ primary alcohol condensed with an average of 7 moles of ethylene oxide per mole.
10	C ₁₂₋₁₅ AE3	: A C ₁₂ -C ₁₅ primary alcohol condensed with an average of 3 moles of ethylene oxide per mole.
	TAED	: Tetraacetyl ethylene diamine
	Silicate	: Amorphorous Sodium Silicate (SiO ₂ :Na ₂ O ratio normally follows)
	CMC	: Sodium carboxymethyl cellulose
15	Zeolite 4A	: Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ SiO ₂) ₁₂ 27H ₂ O having a primary particle size in the range from 1 to 10 micrometers
	Citrate	: Tri-sodium citrate dihydrate
	MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000, available from BASF under the trade name Sokalan CP5.
20	DTPMP	: Diethylene triamine penta (Methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
	Suds	: A mixture of hydrophobic silica and silicone oil.
25	Percarbonate (CO ₃ /SO ₄ coated)	: Anhydrous sodium percarbonate bleach of empirical formula 2Na ₂ CO ₃ .3H ₂ O ₂ coated with a mixed salt comprising Na ₂ CO ₃ and Na ₂ SO ₄ in a molar ratio of 2.5:1, where the weight ratio of percarbonate:mixed salt is 39:1 mean particle size = 550μm
	Savinase	: Proteolytic enzyme sold by Novo Industries A/S
30	Lipolase	: Lipolytic enzyme sold by Novo Industries A/S

		A	B	C	D
35	LAS	7%	7%	7%	-
	C ₁₆₋₁₈ AS	2%	2%	2%	-
	C ₁₄₋₁₅ AS	-	-	-	9%
	C ₁₄₋₁₅ AE7	4%	4%	4%	-
	C ₁₂₋₁₅ AE3	-	-	-	4%
	Silicate 2.0R	4%	4%	4%	4%
40	Copolymer AA/MA	4%	4%	4%	4%
	Zeolite 4A	20%	20%	20%	2%
	Citrate	5%	5%	5%	5%
	Phosphonate - DTPMP	0.4%	0.4%	0.4%	0.3%
	TAED	5%	5%	5%	1%
45	CMC	0.3%	0.3%	0.3%	1.5%
	Suds Suppressor	1%	1%	1%	0.4%
	Savinase (4.0 KNPU/g)	1.5%	1.5%	1.5%	1.5%
	Lipolase (100,000 LU/g)	0.4%	0.4%	0.4%	0.4%
	Sodium Carbonate (anhydrous)	15%	15%	15%	15%
50	Sodium Percarbonate	20%	20%	20%	20%
	Cellulose ether (Methyl hydroxy ethyl cellulose) (Tylose MH50 from Hoechst)	1%	-	-	-
	Cellulose ether (Hydroxypropyl methyl cellulose) (Methocel F4M from DOW)	-	1%	-	1%
55	Cellulose ether (Hydroxybutyl methyl cellulose)	-	-	1%	
	Balance -Moisture/Miscellaneous	100%	100%	100%	100%

Claims

1. A laundry detergent composition comprising:
 - (a) an alkali metal percarbonate
 - (b) one or more non-ionic cellulose derivatives.
- 5 2. A detergent composition according to claim 1 in which said one or more non-ionic cellulose derivatives are present in a total amount of not more than 3% by weight of total composition.
- 10 3. A detergent composition according to claim 2 in which said one or more non-ionic cellulose derivatives are present in a total amount of not more than 1.5%, preferably not more than 1%, by weight of total composition.
- 15 4. A detergent composition according to any preceding claim in which said one or more non-ionic cellulose derivatives are selected from cellulose ethers.
- 5 5. A detergent composition according to claim 4 in which said one or more non-ionic cellulose derivatives are selected from hydroxy ethyl cellulose, hydroxy propyl cellulose, methyl cellulose and mixtures thereof.
- 20 6. A detergent composition according to any preceding claim additionally comprising additional bleaching agents selected from peroxyacid bleach precursors and organic peroxyacids and mixtures thereof.
7. A detergent composition according to claim 6, wherein the additional bleaching agent is TAED.
- 25 8. A detergent composition according to any preceding claim additionally comprising surfactant in an amount of from 3 to 35% by weight of total composition, said surfactant being selected from anionic, cationic, non-ionic, ampholytic and zwitterionic surfactants and mixtures thereof.
- 30 9. A detergent composition according to any preceding claim which is phosphate-free and comprises from 1 to 80% by weight of total composition of non-phosphate detergent builder compounds.
- 10 10. A detergent composition according to claim 9, wherein the non-phosphate detergent builder compounds are selected from crystalline layered sodium silicates and zeolites and mixtures thereof.
- 35 11. A process of washing laundry in a domestic washing machine in which an effective amount of a laundry detergent composition is introduced into the wash liquor during the wash, wherein the process is conducted at a temperature of no more than 50 °C, and wherein the laundry detergent composition comprises:
 - (a) an alkali metal percarbonate
 - (b) one or more non-ionic cellulose derivatives.
- 40 12. A process according to claim 11, wherein the process is conducted at a temperature of between 10 and 35 °C.
- 45 13. A process according to claim 11 or claim 12, wherein the laundry comprises hydrophobic materials.
14. A process according to any of claims 11 to 13, wherein the detergent composition is a composition according to any of claims 2 to 10.

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 508 934 (VIKING INDUSTRIES) * page 11, line 32 - line 36; example 4 * ---	1-5, 7-10	C11D3/39 C11D3/22
X	GB-A-1 534 641 (UNILEVER) * claims 1-4; table 2 * ---	1-5, 8	
X	DATABASE WPI Section Ch, Week 8703, Derwent Publications Ltd., London, GB; Class A97, AN 87-019308 & JP-A-61 278 394 (KAO CO.) 9 December 1986 * abstract * ---	1, 4, 5, 7-10	
X	DATABASE WPI Section Ch, Week 8703, Derwent Publications Ltd., London, GB; Class A97, AN 87-019309 & JP-A-61 278 395 (KAO CO.) 9 December 1986 * abstract * ---	1, 4, 5, 7-10	
A	US-A-4 854 333 (E. INMAN ET AL.) * claims 3,12 * ---	1	C11D
A	FR-A-2 348 963 (THE DOW CHEMICAL COMPANY) * claims 1,5 * -----	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		8 December 1993	Van Bellingen, I
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

